A hierarchical cathode catalyst layer architecture for improving the performance of direct methanol fuel cell

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ARTICLE INFO

ABSTRACT

We report the fabrication of a hierarchical cathode catalyst layer (CL) for application in direct methanol fuel cells (DMFCs). The hierarchical CL, comprised of Pt black as the inner layer and Pt/C as the outer layer, has appropriate structural properties for DMFC cathode. The inner CL with compact structure decreases the CL thickness and prevent Pt sites from methanol contamination, and the cathode outer CL with porous structure increase the electrochemical active surface area. Consequently, the hierarchical cathode CL is able to offset the adverse effect of methanol crossover on the cathode performance by enhancing the Pt catalyst utilization for oxygen reduction reactions (ORR). Therefore, the newly developed membrane electrode assembly (MEA) can maintain the high ORR activity of the cathode catalysts despite the methanol crossover. At a high methanol concentration (3 M), it shows high maximum power density ($0.156 \, \mathrm{W \, cm^{-2}}$) despite only $1.0 \, \mathrm{mg \, cm^{-2}}$ of Pt in the cathode CL.

1. Introduction

The direct methanol fuel cell (DMFC) is an electrochemical device that directly converts the chemical energy of methanol into electrical energy. DMFCs are considered one of the best alternative power sources for future portable electronic devices because of their high energy density ($4.8 \, \mathrm{kWh \, L^{-1}}$), convenient liquid fuel handling, and simple system design [1–3]. However, despite their outstanding potential, DMFC technology is confronted with barriers that need to be overcome before their widespread commercialization [4]. One of these barriers is the methanol crossover from the anode to the cathode through the membrane. The concentration gradient of methanol results in the direct permeation of unreacted methanol from the anode to the cathode, together with water [5,6]. As a result of this crossover, the electrochemical oxidation of permeated methanol can occur on the cathode surface, together with the electrochemical reduction of oxygen, which

causes a mixed potential. Furthermore, the cathode catalyst can be poisoned by carbon containing intermediates of the methanol electro-oxidation reactions (MOR), resulting in decreased oxygen reduction reactions (ORR) [7–9]. Furthermore, methanol crossover exaggerates flooding at the cathode, which limits the mass transport of oxygen [6,10]. Thus, methanol crossover causes a drastic decrease in cathode performance, to overcome which the cathode in DMFCs requires excessive amounts of noble metal catalysts.

Considerable efforts have been made to mitigate the effect of methanol crossover on DMFC performance via membrane modification [11–14], development of highly active anode catalysts for MOR, and methanol tolerant cathode catalysts [15–19]. However, methanol crossover still occurs in the new anode catalysts because the methanol fed into the anode cannot react completely. Besides, most methanol-tolerant catalysts have low catalytic activity for ORR [8]. The issue has not been solved so far by the newly developed membranes either [13,14]. In another approach to solve the methanol crossover problem, changes in the electrode structure of membrane electrode assembly (MEA) have been attempted [20–28]. While most of the studies have mainly focused on the anode, it is also important to develop a new cathode design that can minimize the detrimental effect of the permeated methanol, because it is not possible to completely eliminate methanol crossover [25].

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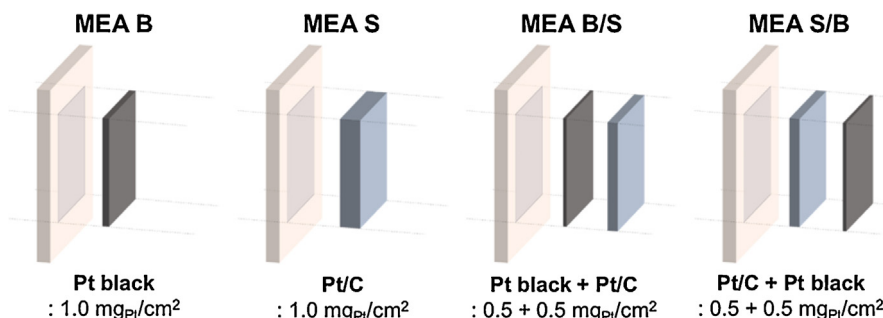[1] These authors contributed equally to this work.

Fig. 1. Schematic illustration of cathode catalyst layer of four different MEAs (MEA B, S, B/S, S/B).

In this study, we propose a hierarchical cathode structure consisting of unsupported Pt (Pt black) as the inner CL and carbon-supported Pt (Pt/C) as the outer CL. The same catalysts function as the CLs in a conventional MEA without any additive such as PtRu [25,27,28], so the only difference here is the cathode structure. Methanol solutions of different concentrations (1 and 3 M) were fed into the anode to examine the effect of methanol crossover. A detailed electrochemical analysis was also carried out to clarify the effect of a hierarchical CL on DMFC performance.

2. Experimental

2.1. MEA fabrication

Catalyst inks were prepared by mixing an appropriate amount of the catalysts with deionized water, isopropyl alcohol, and an ionomer (5 wt. % Nafion solution, Sigma–Aldrich Co.). PtRu black (atomic ratio of Pt:Ru is 1:1, Johnson Matthey Co.) was used in the anode catalyst inks, and Pt-based catalysts (Pt black and 60 wt. % Pt/C, Johnson Matthey Co.) were used in the cathode catalyst inks. The catalyst coated membrane (CCM) was fabricated by directly spraying the catalyst ink onto both sides of Nafion 115 membrane (Dupont), which was pretreated with a 3 wt. % hydrogen peroxide solution for 1 h, followed by a 0.5 M sulfuric acid solution for 1 h. Fig. 1 illustrates the four MEAs having different cathode CLs (MEA B, S, B/S, and S/B). As conventional MEAs with single-layered cathode CL, MEA B, and MEA S had a single-layered cathode CL consisting of Pt black and 60 wt. % Pt/C, respectively, with the same Pt loading of $1.0 \, mg \, cm^{-2}$. The new MEAs (MEA B/S and MEA S/B) contained a hierarchical cathode CL. MEA B/S was fabricated using Pt black as an inner cathode CL and Pt/C (Pt loading of $0.5 \, mg \, cm^{-2}$ in both layers) as an outer cathode CL. In MEA S/B, Pt/C was the inner cathode CL and Pt black (Pt loading of $0.5 \, mg \, cm^{-2}$ in both layers) was the outer cathode CL. PtRu black with a loading of $2.0 \, mg \, cm^{-2}$ was used as the anode CL in all of the CCMs. After the spray coating process, the CCMs were sandwiched between the anode gas diffusion layer (GDL) (TGPH-060-020, Toray Co.) and cathode GDL (35 BC, SGL Co.) without a hot pressing process.

2.2. Physical characterization

Field-emission scanning electron microscopy (FE-SEM) analysis was conducted using a MERLIN Compact (ZEISS) to examine the structure of the surface and cross-section of the cathode CL in the MEAs. A contact angle analyzer (Phoenix 300) was used to investigate the hydrophobicity of the Pt black and Pt/C CLs by detecting the contact angles of water droplets on the surface of the CLs. The CLs were created on the gas diffusion layer (SGL 35BC, micro porous layer on carbon paper with a wet proofing coating) to carry out the contact angle measurements.

2.3. Electrochemical characterization

A single-cell test was carried out to investigate the effect of the hierarchical cathode CL on the DMFC performance. Each fabricated MEA was inserted between two graphite plates that contained serpentine-type flow channels. The single cell was assembled with identical torque and connected to a fuel cell test station (CNL Energy Co.). The active area of the MEA was $5.0 \, cm^2$. Methanol solutions of different concentrations (1 and 3 M) and non-humidified air without back pressure were fed into the anode and the cathode, respectively. The feed rate of the methanol solutions were 3.0 and $0.5 \, mL \, min^{-1}$ at 1 and 3 M, respectively, while the flow rate of air was $200 \, mL \, min^{-1}$. The temperature of the cell was maintained at 70 °C during this operation. Electrochemical impedance spectroscopy (EIS) measurements (IM6, Zahner) of the single cells were conducted at 0.4 V in the frequency range of 0.1 Hz to 10 kHz, with an amplitude of 10 mV, to characterize the electrochemical properties (charge transfer resistance, ohmic resistance, and mass transfer resistance) of the MEAs. The EIS was recorded under the same conditions as the single cell operation.

To further examine the effect of a hierarchical CL on improved Pt utilization for ORR, the iR-corrected cathode polarization curves of each MEA were obtained from the following equation.

$$V_{DMFC \, Cathode, iR}(i) = V_{DMFC \, Full \, Cell, iR}(i) + V_{DMFC \, Anode, iR}(i)$$

The iR-corrected single cell polarization ($V_{DMFC \, Full \, Cell, iR}(i)$) and iR-corrected anode polarization ($V_{DMFC \, Anode, iR}(i)$) of each MEA were calculated by eliminating only the ohmic drop from the polarization curves. The ohmic resistances were measured by EIS. To obtain the iR-corrected cathode polarization curve, the anode polarization curve ($V_{DMFC \, Anode}(i)$) was measured. Methanol solution (1 and 3 M) and humidified hydrogen were supplied to the anode and the cathode, respectively. In this situation, the cathode could be regarded as a dynamic hydrogen electrode (DHE). The anode polarization curve and EIS of each MEA was obtained using the cathode as the reference electrode (RE) and counter electrode (CE) [29–32].

The cathode Pt utilization for ORR was calculated by the following equation.

$$\text{Cathode Pt utilization for ORR} = \frac{V_{DMFC \, Cathode, iR}}{V_{Hydrogen-air, iR}}$$

The cathode Pt utilization for ORR is the ratio of iR-corrected cathode polarization curve of DMFC ($V_{DMFC \, Cathode, iR}$) to the iR-corrected polarization curve of hydrogen–air fuel cell ($V_{Hydrogen-air, iR}$). The hydrogen–air fuel cell is not affected by methanol crossover and the overpotential of hydrogen oxidation reaction can be neglected. Thus, cathode Pt utilization for ORR can indicate the decrease in performance due to permeated methanol. The single-cell performance test and EIS under the hydrogen–air operation were also conducted in the same MEAs.
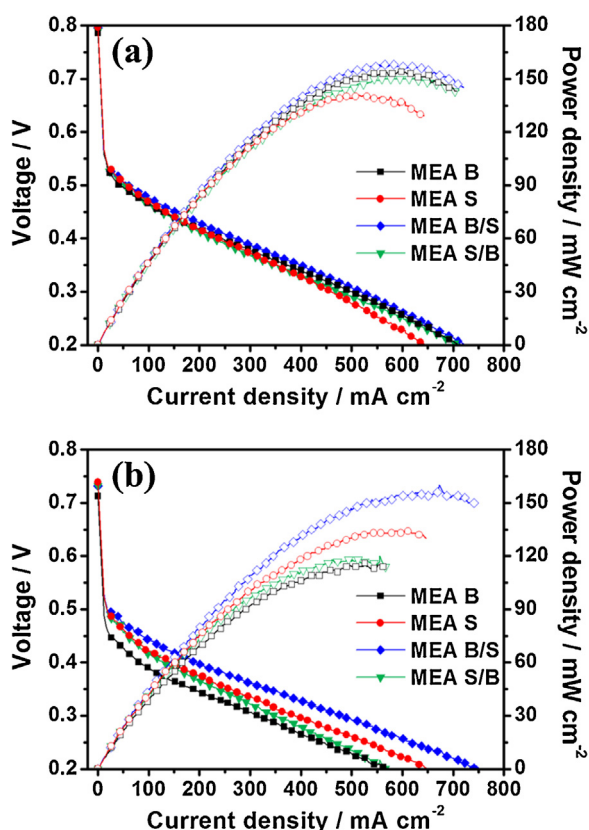
Fig. 2. The single cell polarization curves of the four different MEAs at methanol concentration of (a) 1 M and (b) 3 M.

3. Results and discussion

3.1. Comparison of cell performances of two conventional MEAs

Fig. 2 shows the single cell polarization curves and power density curves of the four MEAs at two representative methanol concentrations (1 and 3 M). The performances of the two conventional MEAs (MEA B and MEA S) are compared to analyze their cathode characteristics. In a direct methanol fuel cell system, the cathode CL can be divided into two sublayers. One is in contact with the polymer electrolyte membrane (PEM) (PEM sublayer, white region in Fig. 3 and the other is in contact with GDL (GDL sublayer, red region in Fig. 3). In the PEM sublayer, concentration of methanol remains high due to the methanol permeated through the PEM, whereas the oxygen concentration is relatively low. Thus, the detrimental effect of mixed potential is significant and ORR activity is very low in this region. On the other hand, in the GDL sublayer, concentration of methanol can be very low or zero (some part of cathode CL very close to the GDL) because most of the permeated methanol is oxidized in the PEM sublayer. In addition, the oxygen concentration remains high because it is close to the GDL. Therefore, ORR dominates in this region and the mixed potential

Cyclic voltammetry (CV) of the two conventional MEAs (MEA B and MEA S) was carried out (scan range: 50 mV to 1.2 V; scan rate: 100 mV s^{-1}) to measure the electrochemical active surface area (ECSA) of two cathode catalysts (Pt black and 60 wt. % Pt/C). Hydrogen was fed into the anode as the reference electrode, and nitrogen was supplied into the cathode as the working electrode. Both gases were fully humidified and the temperature of the single cell was maintained at 30 °C during the measurement.

is significantly reduced. Consequently, maximizing this ORR dominant region is important to enhance DMFC performance [24,27].

At 1 M methanol concentration (Fig. 2(a)), MEA B exhibits higher performance than MEA S in most current density regions (above 0.2 A cm^{-2}). In this condition, the methanol concentration at anode is relatively low when a considerable amount of methanol is oxidized at the anode, so the amount of methanol permeated into the cathode is relatively small. Particularly at high current densities, large amounts of water produced by the ORR at the cathode hinder the oxygen transport, so oxygen mass transport has a greater effect on cathode performance than methanol crossover (Fig. 3(a)). As shown in Fig. 4, thickness of the Pt black layer in MEA B (5.6 μm) is much thinner than that of the Pt/C layer in MEA S (11.8 μm). In addition, MEA B exhibits the higher single cell performance than MEA S under hydrogen–air fuel cell operating condition and it has lower oxygen mass transport resistance (Fig. S1). These results indicate that the thinner Pt black layer of MEA B is advantageous in terms of oxygen transport, which is conducive to DMFC performance in low methanol crossover conditions. As shown in Fig. S2, the higher methanol concentration at the anode leads to the lower open circuit voltage (OCV) related to mixed potential by the methanol crossover. Especially, at 3 M methanol concentration (Fig. 2(b)), MEA S shows higher performance than MEA B in all current density regions. In this severe methanol crossover condition, it is crucial that the surface of the cathode CL is not covered with methanol due to large amounts of permeated methanol by crossover [26]. However, the most of the Pt black layer of MEA B might be contaminated with methanol, the concentration of methanol remains relatively high in the thin CL (Fig. 3 (b)). In contrast, the Pt/C layer of MEA S is thick enough to oxidize the permeated methanol within the part of the CL close to the membrane, and it can retain a considerable amount of Pt catalyst with little or no methanol contamination. In addition, as shown in Fig. S3, the ECSA of the Pt/C layer of MEA S is about twice that of the Pt black layer of MEA B. Hence, the sufficiently thick catalyst layer can hold a considerable amount of the ORR dominant regions and it is less vulnerable to the permeated methanol due to the higher Pt utilization for ORR. Consequently, MEA S is beneficial to high DMFC performance in high methanol crossover condition.

3.2. The effect of hierarchical cathode catalyst layer for DMFC

The current densities at 0.4 V and maximum power densities of each MEA are shown in Table 1. From Table 1 and Fig. S2, it is clear that MEA B/S with its hierarchical cathode structure exhibits the highest single-cell performance among the four types of MEAs in all DMFC operating conditions. When 1 M methanol is used, the performance of MEA B/S is very similar to MEA S at low current densities (below 0.1 A cm^{-2}). Meanwhile, it also shows slightly higher performance than MEA B in the high current density region. This result indicates that decreasing the thickness of the cathode layer (8.8 μm, Fig. 4) leads to lower oxygen mass transport resistance. Furthermore, at higher concentrations (3 M) of methanol, MEA B/S has a much higher performance than two conventional MEAs (MEA B and S) due to its structure which can efficiently mitigate the detrimental effect of methanol crossover. The oxygen diffuses more easily in the entire CL owing to its lower oxygen mass transport resistance, and the permeated methanol can be more effectively oxidized within the compact inner CL of MEA B/S than MEA S. [33] Moreover, as shown in Figs. S4 and S5, the structure of the inner CL (Pt black) has a more hydrophilic surface than the outer CL (Pt/C) due to the absence of carbon support. Lee et al. [26] reported that spatial variation of CL wettability as seen in this structure can reduce methanol crossover by enhancing the back flow of water from the cathode to the anode. Consequently, the permeated methanol can be oxidized in the inner layer of MEA B/S due to
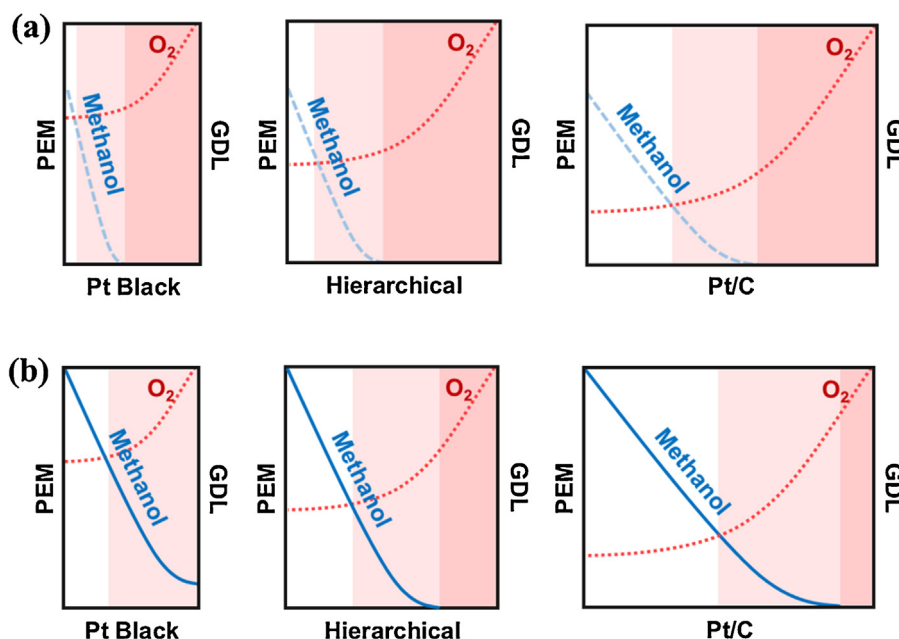
Fig. 3. A schematic diagram illustrating imaginary conditions for three different types of cathode catalyst layers in DMFC; (a) low methanol crossover condition (b) high methanol crossover condition.
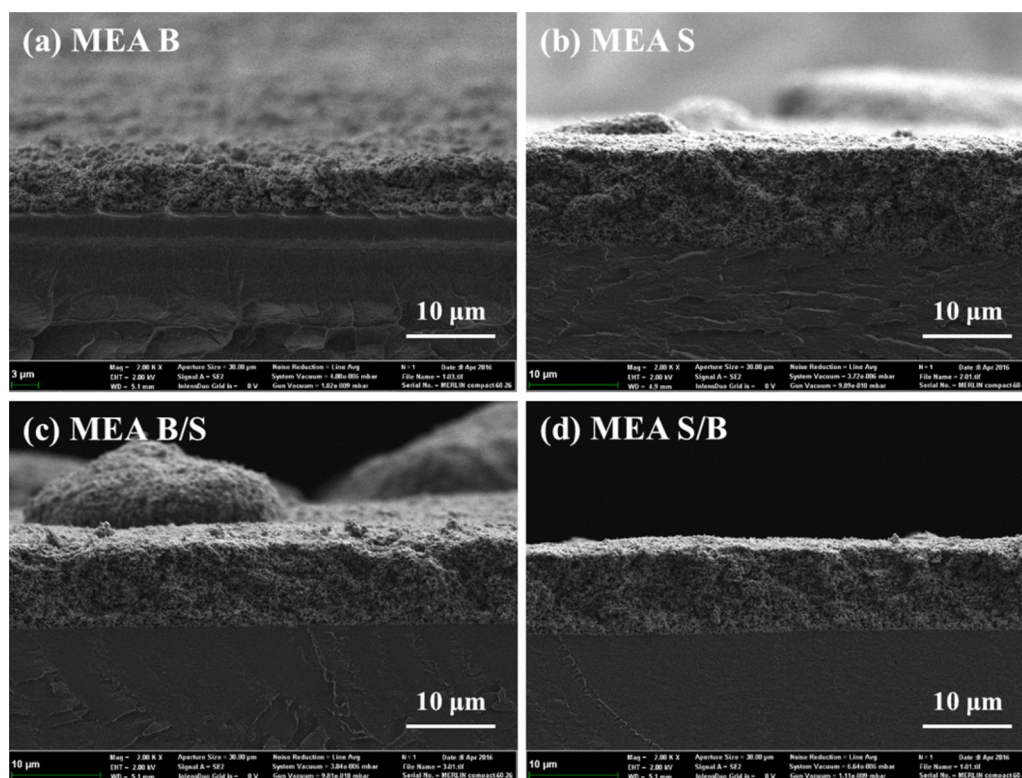

Fig. 4. SEM images of cross-sectional of cathode catalyst layer in four MEAs; (a) MEA B, (b) MEA B, (c) MEA B/S, and (d) MEA S/B.

Table 1
Current density at 0.4 V and maximum power density of each MEA at different methanol concentration (1 M and 3 M).

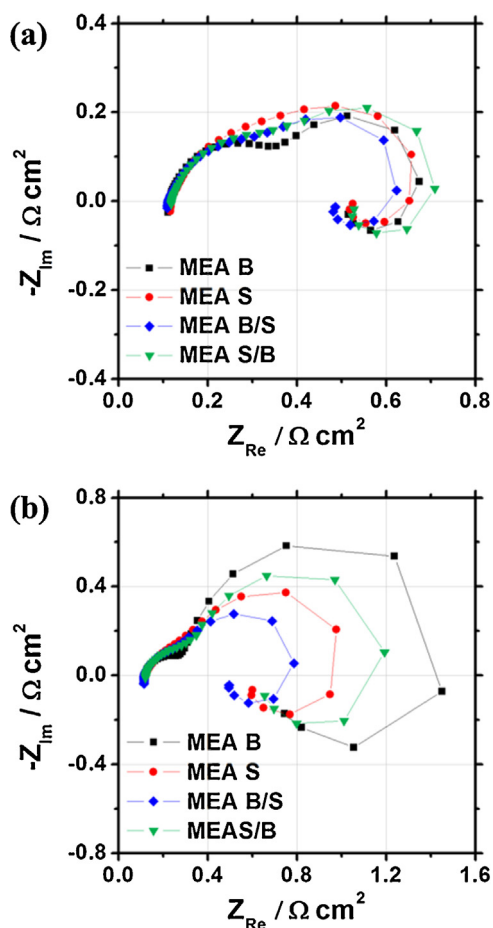| MEAs	1 M methanol		3 M methanol	
	Current density at 0.4 V [A cm^{-2}]	Max. power density [W cm^{-2}]	Current density at 0.4 V [A cm^{-2}]	Max. power density [W cm^{-2}]
MEA B	0.243	0.154	0.082	0.115
MEA S	0.238	0.141	0.143	0.134
MEA B/S	0.270	0.158	0.194	0.156
MEA S/B	0.227	0.151	0.128	0.118

Fig. 5. The EIS curves of four MEAs at 0.4 V in DMFC operation at methanol concentration of (a) 1 M and (b) 3 M.

the lower oxygen mass transport resistance. MEA B/S can also keep more Pt sites in the outer layer (Pt/C) free from methanol contamination, giving the oxygen more opportunities to be reduced on cathode Pt surface. However, despite the same thickness (8.8 μm) of cathode CL as MEA B/S, MEA S/B has a lower performance than the conventional MEAs under certain conditions. Since the catalysts and all the other components were identical, the difference in performance between MEA B/S and MEA S/B could only be attributed to the different structure of cathode CL. As shown in Fig. 3, the ORR activity of the outer CL is higher than that of inner CL because outer layer is mostly free from the detrimental effect of permeated methanol compared to the layer near the membrane. However, the outer CL (Pt black) of MEA S/B has a much lower ECSA than MEA B/S and MEA S. Therefore, despite the lower oxygen mass transport resistance, MEA S/B has a lower cell performance than MEA S in high methanol crossover conditions.

To characterize the electrochemical properties of the four MEAs, the EIS of the MEAs were obtained and the Nyquist plots are shown in Figs. 5(a) and (b). The high-frequency intercept is the ohmic resistance, which is the sum of the ionic and electronic resistances of the cell components. The diameter of the semi-circle at low current densities represents a combination of the charge transfer resistance of the two reactions (MOR and ORR) [32]. It is evident from Fig. 5 that the semi-circles of MEA B/S are the smallest, indicating that MEA B/S has the smallest charge transfer resistance among the four MEAs. Especially, as shown in Fig. 5(b), the charge transfer resistance of MEA B/S is much smaller than the other MEAs at higher methanol concentration. Because MOR activity on the anode might be equal, the decreased charge transfer resistance is attributed only

to ORR activity on the cathode. Thus, the hierarchical cathode CL of the MEA B/S decreases the charge transfer resistance of the DMFC, thereby improving cell performance.

3.3. iR-corrected cathode polarization curves and cathode Pt utilization for ORR

To further demonstrate that MEA B/S can minimize the adverse effect of permeated methanol on the cathode, iR-corrected cathode polarization curves for the four MEAs were obtained. The DMFC polarization curve consists of the anode polarization curve, cathode polarization curve (both iR-corrected), and iR curve [34]. Anode/cathode polarization curves are correlated with the anode/cathode reactions, respectively, and the iR curve is the iR ohmic drop due to the electronic and ionic resistance of the cell components. Thus, comparing the iR-corrected cathode polarizations of the four MEAs is an appropriate method to investigate the effect of CL structure on cathode performance, as the iR-corrected cathode polarization curve is affected only by the cathode reaction. To acquire the iR-corrected cathode polarization curves, the anode polarization curves and iR curves of DMFC are required. First, anode polarization curves ($V_{DMFC\,Anode}(i)$) were obtained using the cathode as a DHE by supplying hydrogen [29–31]. The anode polarization curves and impedance spectra for the four MEAs (Fig. 6) are all analogous to each other because the anodes in the MEAs have the same catalyst. These results confirm that the difference in cell performance (Fig. 2) can be attributed to the cathode and hence the different structures of cathode CL alone. The summation of the iR-corrected anode polarization curves ($V_{DMFC\,Anode,iR}(i)$) and the iR-corrected single-cell polarization curves ($V_{DMFC\,Full\,cell,iR}(i)$) of each MEA (Fig. 7) yields the iR-corrected cathode polarization curves ($V_{DMFC\,Cathode,iR}(i)$). Fig. 7 indicates that MEA B/S has the highest iR-corrected cathode performance, which is consistent with the results shown in Fig. 2.

To clarify the effect of a hierarchical MEA on the cathode performance, the cathode Pt utilization for ORR is calculated. The cathode Pt utilization is the ratio of the iR-corrected cathode voltage between two operations (methanol–air and hydrogen–air). The comparison of the iR-corrected cathode polarization curves of the DMFCs with those of hydrogen–air fuel cells shows the difference between the cathode performance with and without methanol crossover. The iR-corrected cathode polarization curves under hydrogen–air fuel cell operation can be acquired by eliminating the ohmic drop alone from the polarization curve, since the effect of hydrogen oxidation reactions (HOR) can be ignored due to its fast kinetics. The ohmic resistance was measured by EIS and the iR-corrected polarization curves are shown in Fig. 8. In the hydrogen–air fuel cell operation, the performances are similar at low current densities because the effect of methanol crossover is absent. Since all cathode Pt catalysts are utilized for ORR in hydrogen–air operation, the cathode Pt utilization can be defined as the ratio of the iR-corrected cathode voltage between two operations. It can indicate how much of the cathode Pt catalysts were free from permeated methanol. Fig. 9 shows the cathode Pt utilization for the ORR of each MEA. MEA B/S has the highest Pt utilization at all methanol concentrations and the Pt utilization is directly related to the cathode performance.

4. Conclusion

In this study, the hierarchical structure, comprised a Pt black and Pt/C, is applied as the cathode in a DMFC. MEA B/S with a hierarchical cathode structure comprised of Pt black as an inner CL and Pt/C as an outer CL has the highest single cell performance among the four MEAs at all methanol concentrations. Since the four MEAs
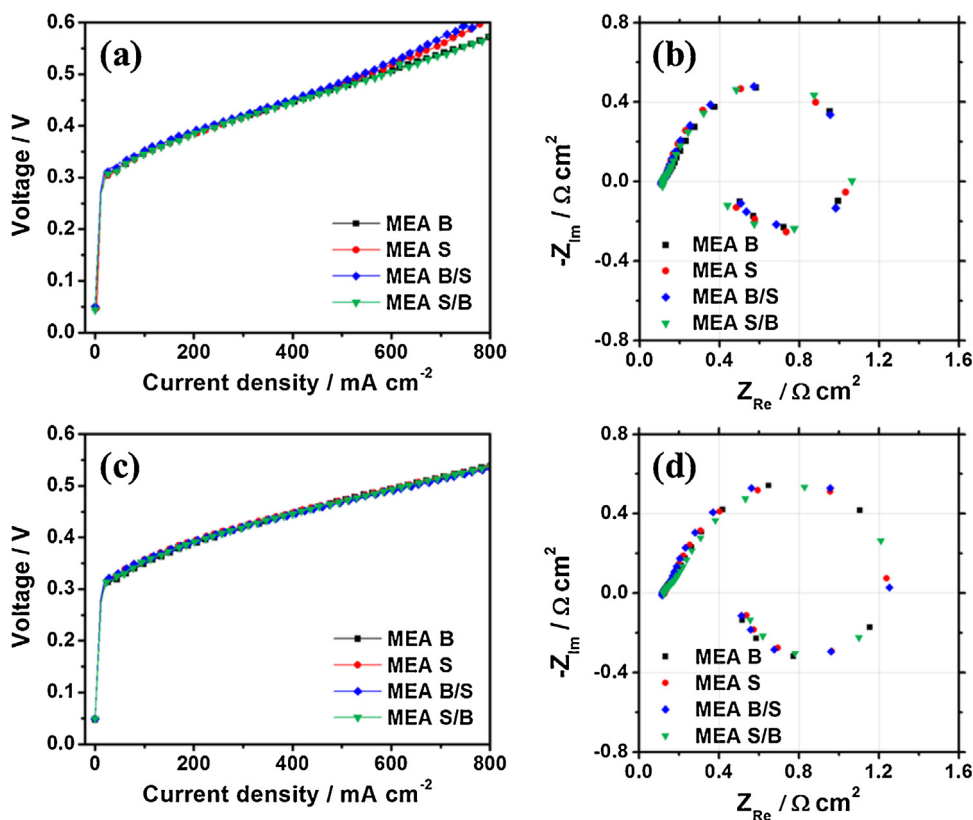
Fig. 6. The anode polarization curves and EIS curves of four MEAs at 0.1 A cm^{-2}. (a), (b) 1 M methanol, and (c), (d) 3 M methanol.
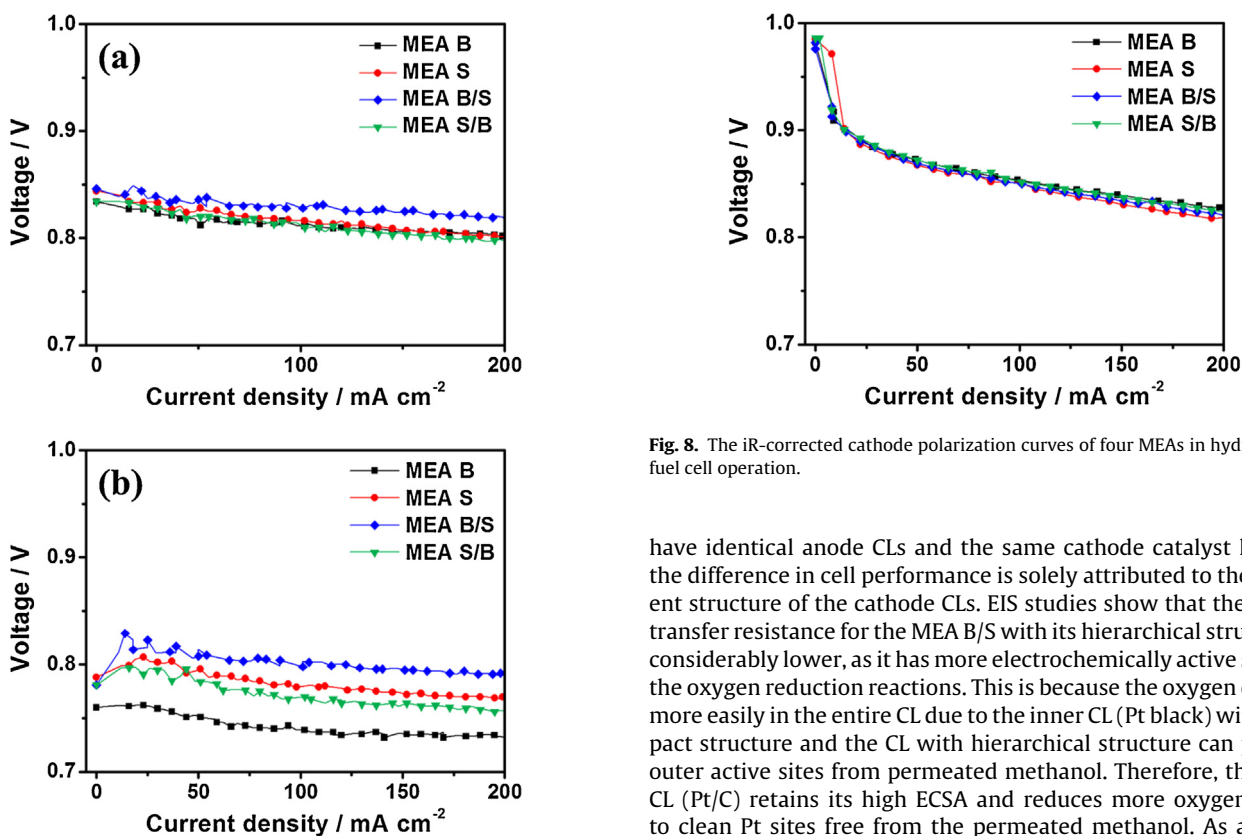

Fig. 7. The iR-corrected cathode polarization curves of four MEAs at methanol concentration of (a) 1 M and (b) 3 M.

Fig. 8. The iR-corrected cathode polarization curves of four MEAs in hydrogen–air fuel cell operation.

have identical anode CLs and the same cathode catalyst loading, the difference in cell performance is solely attributed to the different structure of the cathode CLs. EIS studies show that the charge transfer resistance for the MEA B/S with its hierarchical structure is considerably lower, as it has more electrochemically active sites for the oxygen reduction reactions. This is because the oxygen diffuses more easily in the entire CL due to the inner CL (Pt black) with compact structure and the CL with hierarchical structure can prevent outer active sites from permeated methanol. Therefore, the outer CL (Pt/C) retains its high ECSA and reduces more oxygen owing to clean Pt sites free from the permeated methanol. As a result, the MEA B/S has the highest cathode Pt utilization and the hierarchical structure of MEA B/S is very effective for minimizing the adverse effect of methanol crossover on cathode performance. So, the MEA B/S shows outstanding performance (0.158 W cm^{-2} at 1 M
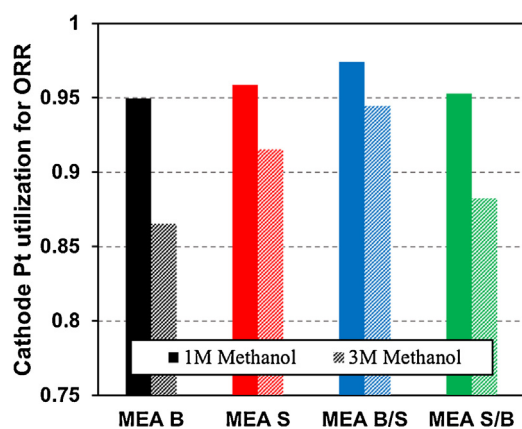
Fig. 9. The cathode Pt utilization for ORR of four MEAs.

and 0.156 W cm^{-2} at 3 M) despite low Pt loading (1.0 mg cm^{-2}) in the cathode CL.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.02.039.

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